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The thermal effect of melting in polycrystalline systems

V.V. Gusarov

Department of High-Temperature Materials Science and Technology, St. Petersburg Technological State Institute (Technical University), 198013 St. Petersburg, Russia

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Abstract

The process of melting in polycrystalline systems based on a single crystalline phase is studied. The thermodynamic inhomogeneity of such systems is demonstrated. In polycrystalline systems the onset of melting takes place at temperatures substantially lower than the melting point; it can be treated as a sequence of transformations, namely the melting of grain-boundary and surface (non-autonomous) phases, and the transition of the crystalline (solid-state autonomous) phase into a non-autonomous liquid phase.

A mathematical model is constructed describing the temporal distribution of the thermal effect of melting as a function of the thermodynamic and kinetic properties characterizing autonomous and non-autonomous phases of the system, the mean grain size, and the sample heating rate. An effect, known as pre-melting in the literature, is described quantitatively.

Modes of thermal analysis are described that, by allowing for the grain size, ensure the most accurate determination possible of the melting temperatures of the autonomous and non-autonomous phases.

Keywords: OSC; DTA; Melting; Model; Polycrystalline system

1. Introduction

Research devoted to differential thermal analysis (DTA) and differential scanning calorimetry (DSC) pay considerable attention to analyzing the shapes of peaks associated with melting, crystallization, other phase transitions, and chemical reactions. Investigation of the effect that instrumental factors and kinetic characteristics of the system under study has on the peak shape enables one to enhance substantially the precision and informational yield of DTA and DSC data [1].

Peak shape is greatly affected by the chemical and phase composition of the sample. When phase diagrams of multi-component and multi-phase systems are constructed on the basis of DTA and DSC results, it becomes a matter of paramount importance to allow for the impact that the sample's chemical and phase inhomogeneities has on the peak shape [2–5]. However, systems consisting of one component and one crystalline phase are not thermodynamically homogeneous either. The indicated inhomogeneities are more pronounced in polycrystalline samples. Sites of contact between grains differing in orientation give rise to transient areas.

When their state is close to equilibrium, we will use the terms suggested by Defay and Prigogine [6] and call the areas local-equilibrium two-dimensional non-autonomous phases. It has been demonstrated [7–11] that the melting points of local equilibrium two-dimensional non-autonomous phases differ from those of autonomous phases. The relationship between these temperatures can be presented as [9]

$$T_{m2-n} = \gamma T_m \quad (1)$$

where T_m is the melting point of autonomous phase in K, T_{m2-n} the melting point of the local-equilibrium two-dimensional non-autonomous phase in K, and γ a dimensionless parameter depending on the enthalpic and entropic characteristics of the phases; its magnitudes are similar for the same type of substances: inorganic oxides, $\gamma = 0.65 \pm 0.1$; organic crystals, $\gamma = 0.55 \pm 0.1$; metals, $\gamma = 0.45 \pm 0.15$.

The fact that at $T \geq T_{m2-n}$ local-equilibrium two-dimensional non-autonomous phases in a polycrystalline systems are liquid is confirmed by diffusion data. From experimental data analysis, it has been demonstrated [12] that the temperature dependences of the diffusion coefficients for metal melts and two-dimensional non-autonomous phases (grain-boundary and surface diffusion) are virtually the same. As has been shown in a number of studies [7,10,13–15], the non-translational size (thickness) of local-equilibrium two-dimensional non-autonomous phases (h_c) is a function of temperature. Using the equation for $h_c(T)$ proposed in Ref. [15], and restricting oneself to the $T \geq T_{m2-n}$ region, it is possible to present the temperature dependence of the thickness of local-equilibrium two-dimensional non-autonomous phases in polycrystalline systems as follows.

$$h_c(T) = \left(\frac{a}{1 - T/T_m + \delta(T)} \right)^{1/n} \quad (2)$$

where a and n are certain weakly temperature-dependent parameters, $\delta(T)$ is a small value satisfying the conditions $\delta(T) > 0$, $\delta(T_m) = \delta_0 \ll 1$.

The physical meaning of the indicated parameters is explained in Ref. [15], where it is shown that one can take $n = 3$ for a number of cases. Analysis of Eqs. (1) and (2) proves that the melting of a polycrystalline system can be represented as a process involving the emergence of a liquid non-autonomous phase at $T = T_{m2-n}$, and the fraction of the liquid local-equilibrium two-dimensional non-autonomous phase increasing with the temperature can be represented as melting being treated as autonomization of the liquid two-dimensional non-autonomous phase.

This way of describing the mechanism of the phase transitions occurring in a one-component system composed of a single crystalline phase when the temperature increases to $T \geq T_m$ explains the effect of pre-melting, which virtually always manifests itself on DTA and DSC curves. Constructing a quantitative model of melting within the framework of these concepts will reveal the influence exerted on the characteristics of DTA and DSC curves, not only by the chemical and phase composition, but also by the degree of system dispersion.

2. Theoretical modeling

For simplicity's sake, consider a polycrystalline system composed of grains of isometric shape and roughly the same size. At temperatures $T > T_{m2-n}$ the volume fraction of two-dimensional non-autonomous phases in the system can be expressed as

$$v(T, t) \simeq 1 - (1 - h(T, t)/d)^3 \quad (3)$$

where t is time, $h(T, t)$ the thickness of the liquid two-dimensional non-autonomous phases under dynamic conditions, and d is the mean grain size. With respect to the parameter $v(T, t)$, the differential thermal effect caused by the substance undergoing transition from the autonomous phase into the liquid two-dimensional non-autonomous phase can be written in the following way

$$q(T, t) = Q(T) \frac{dv(T, t)}{dt} = Q(T) \left[\frac{\partial v(T, t)}{\partial T} w(t) + \frac{\partial v(T, t)}{\partial t} \right] \quad (4)$$

where $Q(T)$ is the thermal effect of transition into liquid two-dimensional non-autonomous phase undergone by a unit volume of solid autonomous phase, and $w(t) = dT/dt$, is the heating rate.

In order to determine the temporal distribution of a melting thermal effect in a general case, it is necessary to have an equation linking the dynamic and the local-equilibrium thicknesses of the two-dimensional non-autonomous phase. It was shown in Ref. [16] that one can utilize the expression

$$v = v_0(T) \left(\frac{h_e(T) - h(T, t)}{h_e(T)} \right)^\alpha \quad (5)$$

where v_{tr} is the rate of transition of autonomous phase to liquid two-dimensional non-autonomous phase, and $v_0(T)$ and α are parameters [16]. Solving the equation set (2)–(5) for various rates of temperature increase, $w(t)$, one can obtain the temporal distribution of the thermal effect of melting in a polycrystalline system.

In the case of low heating rates, i.e. when at any given moment the system state is close to equilibrium ($h(T, t) \simeq h_e(T)$), and for a constant rate of temperature increase ($w(t) = \text{const}$), the most common DTA mode, equation set (2)–(5) yields an analytical solution

$$q(t) = Qw \left(\frac{a^{1/n}}{d(1 - wt + \delta_0)^{1/n}} \right)^2 \frac{3a^{1/n}}{nd(1 - wt + \delta_0)^{1 + 1/n}} \quad (6)$$

Expression (6) was obtained assuming $\delta(T) \simeq \delta_0$. Such an assumption can be validated by the fact that in the present work we are interested in the temperature region close to the melting point ($T \rightarrow T_m$).

3. Results and discussion

In Fig. 1 we present the results of numerical calculations describing the distribution of the differential thermal effect of polycrystalline system melting as a function of grain size. As can be seen from the data obtained, the thermal effect of melting (pre-melting, if we are to use the traditionally recognized terms [17]) polycrystalline inorganic oxides of grain size $\approx 1 \mu\text{m}$ is clearly apparent even at temperatures $T \approx 0.95T_m$. Reduction of the grain size to submicron dimensions ($\approx 0.1 \mu\text{m}$) shifts the temperature of the thermal effect manifestation down to $T \approx 0.85T_m$. In this case we observed a substantial shifting of the maximum heat consumption intensity $T_{\text{max}} \approx 0.968T_m$, with the melting process coming to completion at $T \approx 0.98T_m$. A decrease in grain size down to dimensions commensurate with $h_c(T_{m2-n}) \approx 1-10 \text{ nm}$ leads to the melting point approaching $T = T_{m2-n}$.

Two kinetic processes resulting in distortion of the profile of the $q(t)$ dependence curve are ignored in model (6) describing the thermal effect of melting. At high heating rates the system cannot be considered a local equilibrium one at any time. In this case it is the equation set (2)–(5) that constitutes the model. At low heating rates one must allow for recrystallization processes taking place with extra intensity in the case of small grain sizes. Fig. 2 illustrates the changes undergone by the $q(t)$ profile in the latter case.

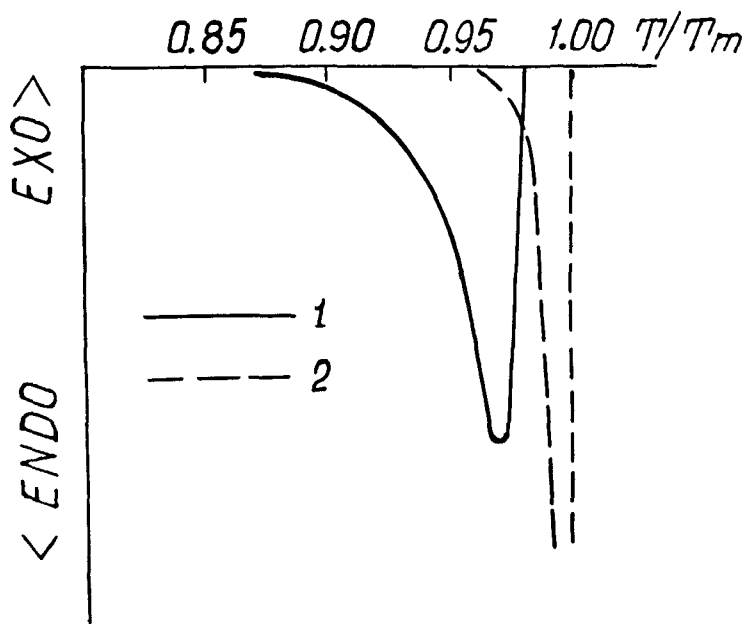


Fig. 1. Distribution of the relative differential thermal effect of polycrystalline system melting as a function of relative temperature T/T_m for various mean grain sizes d : 1, $d = 0.1 \mu\text{m}$; 2, $d = 1.0 \mu\text{m}$. Calculations performed for the following values of Eq. (6) parameters: $\delta_0 = 0.35 \times 10^{-6}$, $n = 3$, $a = 0.35 \text{ nm}^3$ (T_m , melting temperature of the autonomous phase).

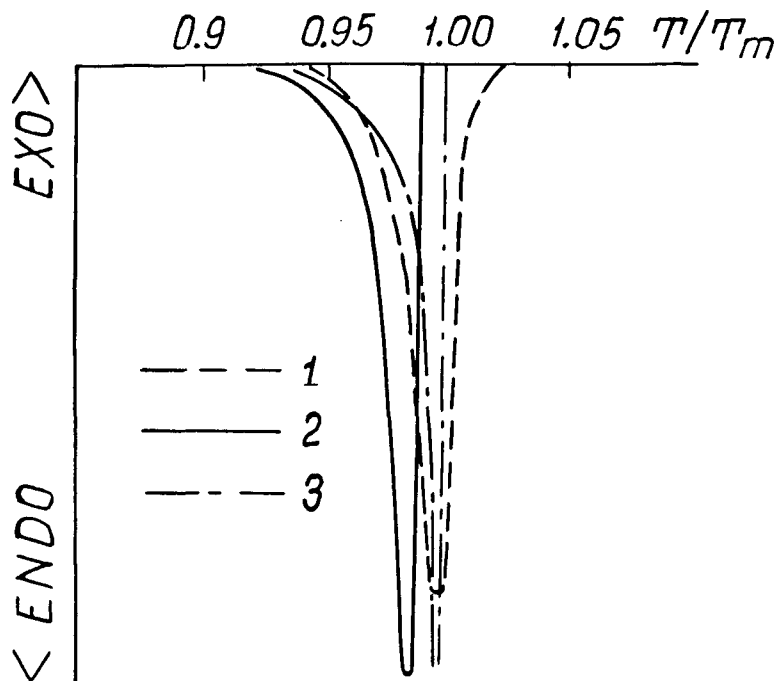


Fig. 2. Differential thermal effect of polycrystalline sample melting (mean grain size $d = 0.2 \mu\text{m}$), calculated on the basis of: 1, models (2)–(5); 2, model (6); 3, model (6) with grain growth accounted for.

The results obtained in the present work demonstrate that it is necessary to use either single-crystal samples, or polycrystals with a grain size d in the range 10–100 μm in order to determine the T_m value by means of DTA and DSC. When samples of smaller grain size are utilized, the rate of temperature increase should be as low as possible during the course of the thermal analysis. In this case the melting point (T_m) can be identified either as the minimum point of the $q(t)$ dependence curve, or as the point corresponding to the second time when the $q(t)$ curve touches the base line, because in the case under consideration these two points practically coincide. We should also note that we did not consider instrumental distortions which make the registered thermal effect smear and shift in accordance with a well-known DTA equation [1].

Determination of the temperature T_{m2-n} can be performed by applying DTA and DSC techniques to nanopowders, and in some cases even to samples of submicronic grain dimensions. The temperature increase rate should be sufficiently high to prevent recrystallization.

References

- [1] J. Šesták, *Thermophysical Properties of Solids. Their Measurements and Theoretical Thermal Analysis*, Academia, Prague, 1984.
- [2] R. Courchinoux, N. B. Chanh, Y. Haget, E. Tauler and M.A. Cuevas-Diarte, *Thermochim. Acta*, 128 (1988) 45.
- [3] S. Sarge, S. Banerecker and H.K. Cammenga, *Thermochim. Acta*, 129 (1988) 309.

- [4] R. Courchinoux, N.B. Chanh, Y. Haget, T. Calvet, E. Estop and M.A. Cuevas-Diarte, *J. Chem. Phys.*, 86(3) (1989) 561.
- [5] T. Calvet, E. Tauler, M.A. Cuevas-Diarte, J.R. Housty, D. Mondieiy, Y. Haget and J.C. Van Miltenburg, *Thermochim. Acta*, 204 (1992) 271.
- [6] R. Defay and I. Prigogine, *Tension superficielle et adsorption*, Éditions Desoer, Liège, 1951.
- [7] R. Kikuchi and J.W. Cahn, *Phys. Rev. B*, 21 (5) (1980) 1893.
- [8] J. Broughton and G.H. Gilmer, *J. Chem. Phys.*, 79 (1983) 5095, 5105, 5114.
- [9] V.V. Gusarov and S.A. Suvorov, Phase generation and material properties in systems $\text{BeO}-\text{AlO}_{1.5}-\text{MeO}_n$ (Me – 3d element, Ga) (in Russian), Leningrad (1988), Scientific-Research Institute of Technical and Economic Investigations of the Chemical Industry (ONIITEKKhIM), Cherkassy, deposited paper No 787-khp-88, 1988.
- [10] J.G. Dash, *Contemp. Phys.*, 30 (1989) 89.
- [11] V.V. Gusarov and S.A. Suvorov, *Zh. Prikl. Khim.* (English transl. in *Russ. J. Appl. Chem.*), 63 (1990) 1689.
- [12] W. Gust, S. Mayer, A. Bogel and B. Predel, *J. Phys. C4*, 46 (1985) 537.
- [13] A. I. Rusanov, *Phase equilibria and surface phenomena* (in Russian), Khimiya, Leningrad, 1967.
- [14] D.R. Clarke, *J. Am. Ceram. Soc.* 70 (1987) 15.
- [15] V.V. Gusarov and S.A. Suvorov, *Zh. Prikl. Khim.* (English transl. in *Russ. J. Appl. Chem.*), 66 (1993) 1529.
- [16] V.V. Gusarov and S.A. Suvorov, *Zh. Prikl. Khim.* (English transl. in *Russ. J. Appl. Chem.*), 65 (1992) 1478.
- [17] E.I. Rabkin, L.S. Shvindlerman and B.B. Straumal, *J. Less-Common Metals*, (1990) 158, 23